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(54) Title: METHODS AND COMPOSITIONS FOR PROTECTING POLYMERS FROM UV LIGHT (57) Abstract A polymeric article, such as an extruded or molded article or a biaxially oriented tape or film, and a method of stabilizing such a polymeric article to protect the article from degradation due to exposure to UV light. The article is formed by blending a polymeric material with from about 50 to about 5,000 ppm of at least one ortho hydroxy tris-aryl triazine light absorber and from about 500 ppm to about 1.25 percent of at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, to form a stabilized polymeric composition, and forming an extruded or molded article or a biaxially oriented tape or film from the stabilized polymeric composition.		

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**METHODS AND COMPOSITIONS FOR PROTECTING
POLYMERS FROM UV LIGHT**

FIELD OF THE INVENTION

5 The invention is directed to compositions and a method of protecting polymeric materials from ultraviolet radiation or light ("UV light"). In particular, the invention relates to polymeric articles comprising synergistic combinations of at least one ortho-hydroxy tris-aryl-triazine UV light absorbers and at least one oligomeric, polymeric, or high molecular weight hindered amine light stabilizers ("HALS").

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BACKGROUND OF THE INVENTION

 It is well-known that UV light or radiation, particularly from sunlight, can cause the degradation of polymers. Often, this results in the embrittlement or yellowing of polymers, which may be in the form of molded articles, polymer films, tapes, coatings, and
15 the like. However, this degradation can be inhibited by the incorporation of ultra-violet light stabilizers and ultra-violet light absorbers in or on such articles.

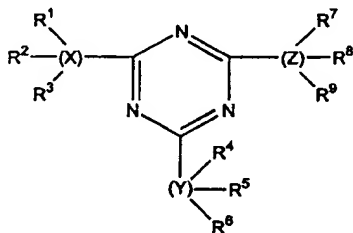
 The use of HALS and UV light absorbers ("UVA"), both individually and in combination, to stabilize polymeric materials is generally known in the art. In particular, UV
20 light absorbers such as benzotriazoles and benzophenones were initially used to stabilize polymeric materials, and to prevent the degradation of such materials from exposure to UV light. Later, it was discovered that HALS, which scavenge free radicals formed in the polymeric material when exposed to UV light, were more effective than UV light absorbers, and thus, UV light absorbers are presently used in combination with at least one HALS in most conventional applications.

25 European Patent Application No. EP 0 704 560 discloses pigmented fiber of no more than 50 microns thick, in which the pigment is stabilized with a synergistic mixture of a HALS and a UV light absorber. The application discloses that the amount of both the HALS and the UV light absorber that is effective in stabilizing the pigment in the fiber is 0.05 to 5 percent by weight, but provides examples that show no significant improvement
30 when the amount of HALS is increased over the amount of UV light absorber.

 European Patent No. EP 0 453 396 discloses coating compositions containing from 0.01 to 5 percent by weight of a mixture of UV light absorbers containing at least one 2-hydroxyphenyl benzotriazole and at least one 2-hydroxyphenyltriazine or 2-hydroxybenzophenone, where the UV light absorbers are present in the molar ratio of
35 3:1 to 1:3. Optionally, the coating composition may contain a derivative of a polyalkylpiperidine HALS, such as 2,2,6,6-tetramethylpiperidine. Although a number of

such polyalkylpiperidine derivatives are disclosed in EP 0 453 396, the amount of HALS useful in the claimed composition is not disclosed, and none of the examples specifically disclose a composition containing a HALS. All examples show some degradation after 1,000 to 2,000 hours of exposure to a Xenon Weatherometer, or after exposure to the sun in Florida for a period of about one year.

U.S. Patent No. 4,619,956 discloses a method of stabilizing a polymer film, coating, or molded article against the action of light, moisture, and oxygen. The method comprises incorporating a HALS and a tris-aryl-2-triazine UV light absorber into the polymer. Preferably, the HALS is a 2,2,6,6-tetralkylpiperidine compound, salt, or metal complex, and the UV light absorber is a tris-aryl-2-triazine of formula



where X, Y, and Z are each aromatic, carbocyclic groups, and at least one of the aromatic groups has a hydroxy group ortho to the point of attachment to the triazine ring. Each of R¹ to R⁹ is hydrogen, hydroxy, alkyl, alkoxy, sulfonic, carboxy, halo, haloalkyl, or acylamino. Each of the UV light absorbers and HALS are used in an amount of from about 0.01 to about 5 percent by weight, but only formulations having equal amounts of UV light absorber and HALS are exemplified. The compositions are effective in stabilizing the polymeric material, which does not begin to lose gloss or turn yellow until after about 1,000 to about 2,400 hours of exposure to UV light.

U.S. Patent No. 4,331,586 to Hardy discloses oligomers for use as light stabilizers. While providing protection for polymeric materials such as polypropylene, polymeric films containing the disclosed oligomeric HALS became brittle after exposure to UV light for about 1,700 hours.

Therefore, a need remains for compositions and methods of use thereof that stabilize polymeric materials and provide protection from exposure to UV light for extended periods of time. The present invention provides such methods and compositions.

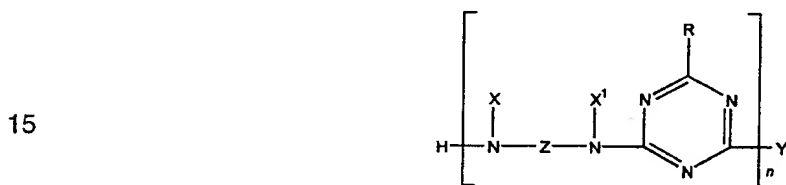
SUMMARY OF THE INVENTION

The present invention is directed to polymeric articles, such as molded articles, extruded articles, and biaxially oriented tapes and films, where the article comprises a polymeric material, from about 50 to about 5,000 ppm of at least one ortho

5 hydroxy tris-aryl triazine light absorber and from about 500 ppm to about 1.25 percent of at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine is from about 3:1 to about 20:1, preferably, from about 5:1 to about 10:1, and most preferably from about 6:1 to about 7.5:1. Preferably, the polymeric article is a molded or extruded article having a

10 thickness of no less than about 1 mm.

HALS useful in the invention include oligomers of formula (I)



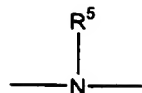
wherein R is morpholino, C₁-C₈ alkylamine, di(C₁-C₈) alkylamine, pyrrolidyl, or

20 cyclohexylamine, X and X', which are the same or different, and are hydrogen, C₁-C₂₀ alkyl, or a radical of formula (II)

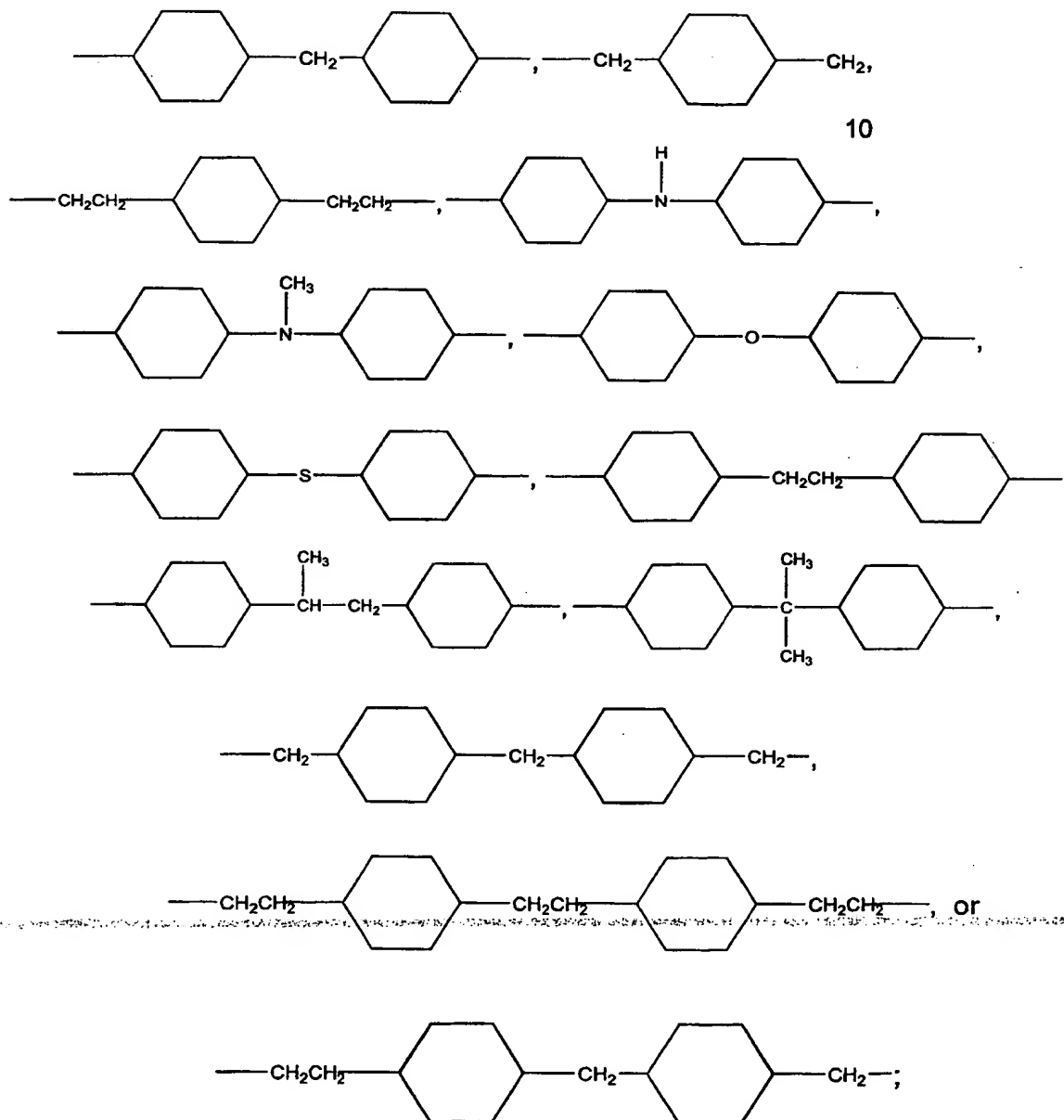


30 wherein R¹ represents hydrogen, C₂-C₃ hydroxyalkyl, C₁-C₈ alkyl, hydroxyl, or oxyl; R² represents hydrogen, C₁-C₈ alkyl, or benzyl; R³ and R⁴, are the same or different, and are C₁-C₈ alkyl, benzyl, or phenethyl, or from a C₅-C₁₀ cycloalkyl; Z is a straight chained or branched C₂-C₂₀ alkylene or a straight chained or branched C₂-C₂₀ alkylene chain interrupted by at least oxy, thio, or

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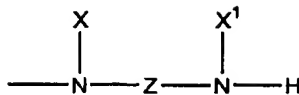


5 radical, wherein R⁵ is hydrogen, C₁-C₂₀ alkyl, or the radical of formula (II); C₅-C₁₀ cycloalkylene,



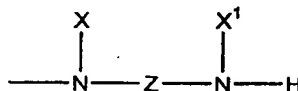
35 C₆-C₁₂ aryl n , or C₈-C₁₄ aralkyl ne; n is an int g r greater than 1; and Y is a halogen atom, C₁-C₈ alkylamine, di(C₁-C₈) alkylamin , pyrrolidyl, morpholino, cyclohexylamine, or

5



wherein X, X¹, and Z are as previously defined; with the proviso that at least one of X and X¹ is of formula (II). Most preferably, X and X¹ are the same or different, and are of formula (II), wherein R is morpholino or octylamine, R¹ is H or CH₃, R² is H, R³ and R⁴ are
 10 CH₃, Z is C₆H₁₂, and Y is morpholino, octylamine, or

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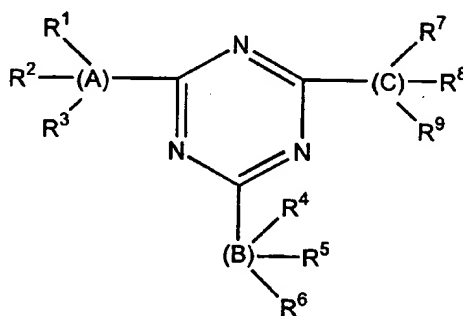
wherein X, X¹, and Z are as previously defined.

Other HALS useful in the invention include, but are not limited to the following:

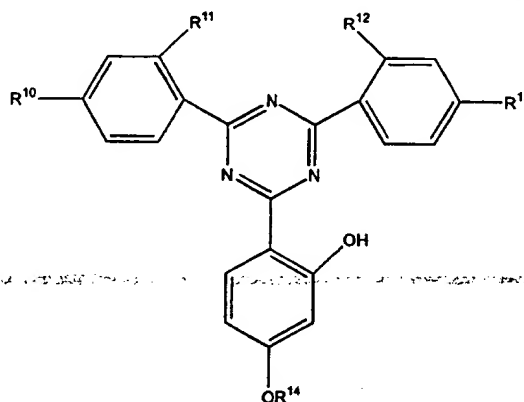
- 20 1. Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidiny)sebacate
2. Dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol
3. A blend of dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol and N,N-bis(2,2,6,6-tetramethyl-4-piperidiny)-1,6-hexane diamine, polymer with
- 25 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentamine
4. 1,3,5-triazine-2,4,6-triamine, N,N==[1,2-ethanediylbis [[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazine-2-yl]imino]-3,1propanediyl]]-bis[N=N--dibutyl-N,N==bis(1,2,2,6,6-pentamethyl-4-piperidiny)]
5. 1,3,5-triazine-2,4,6-triamine, N,N==[1,2-ethanediylbis
- 30 [[[(4,6-bis[butyl(1-cyclohexyloxy-2,2,6,6-tetraamethyl-4-piperidiny)amino]-1,3,5-triazine-2-yl]imino)-3,1-propanediyl]]-bis[N=N--dibutyl-N,N==bis(1,2,2,6,6-pentamethyl-4-piperidiny)]
6. 1,3,5-triazine-2,4,6-triamine, N,N==[1,2-ethanediylbis [[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-2-yl]imino]-3,1propanediyl]]-bis[
- 35 N=N--dibutyl-N,N==bis(1,2,2,6,6-pentamethyl-4-piperidiny)]

7. N,N-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexane diamine polymer with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentamine
8. Poly-methylpropyl-3-oxy-(4(2,2,6,6-tetramethyl) piperidiny) siloxane
9. Poly-methylpropyl-3-oxy-(4(1,2,2,6,6-pentamethyl) piperidiny)siloxane
10. Polyalkyl-1-oxa-diazaspirodecane products of a reaction of tetramethyl-7-oxa-3,20-diaza-21-oxo-dispiro (5.1.11.12)heneicosane with epichlorohydrin
11. 1,3-propanediamine,N,N=-1,2-ethanediylbis-,polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-2,2,6,6-tetramethyl-4-piperidinamine.

Typically, the triazine light absorber is of formula (III)



wherein A, B and C are each aromatic, at least one of A, B and C is substituted by a hydroxy group ortho of the point of attachment to the triazine ring, and each of R¹ through R⁹ is selected from the group consisting of hydrogen, hydroxy, alkyl, alkoxy, sulfonic, carboxy, halo, haloalkyl and acylamino. Preferably, the triazine light absorber is of formula (IV)



where R¹⁰, R¹¹, R¹² and R¹³ are the same or different, and are individually selected from the group consisting of hydrogen, hydroxy, alkyl, alkoxy, sulfonic, carboxy, halo, haloalkyl and acylamino, and R¹⁴ is hydrogen or C₁ to C₁₈ alkyl. Most preferably, R¹⁰, R¹¹, R¹² and R¹³ are H or CH₃, and R¹⁴ is hydrogen, C₆H₁₃, or C₈H₁₇.

Other useful triazine light absorbers include, but are not limited to

2-(4,6-Diphenyl-1,3,5-triazine-2-yl)-5-(hexyl)oxy-phenol,
 2-(4-((2-hydroxy-3-dodecyloxypropyl)-oxyl-2-hydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,
 3,5-triazine, 2-(4-((2-hydroxy-3-tridecyloxypropyl)-oxyl-2-hydroxyphenyl)-
 5 4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,
 2-(4-((2-hydroxy-3-tridecyloxypropyl)-oxyl-2-hydroxyphenyl)-
 4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, and
 2-(4-((2-hydroxy-3-isooctyloxypropyl)-oxyl-2-hydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,
 3,5-triazine, and blends thereof.

10 The light stabilized polymeric article may be formed from a polymeric
 material, such as any of a polyolefin, polyester, polyether, polyketone, polyamide, natural
 or synthetic rubber, polyurethane, polystyrene, high-impact polystyrene, polyacrylate,
 polymethacrylate, polyacetal, polyacrylonitrile, polybutadiene, polystyrene, ABS, SAN
 (styrene acrylonitrile), ASA (acrylate styrene acrylonitrile), cellulosic acetate butyrate,
 15 cellulosic polymer, polyimide, polyamideimide, polyetherimide, polyphenylsulfide, PPO,
 polysulfone, polyethersulfone, polyvinylchloride, polycarbonate, polyketone, aliphatic
 polyketone, thermoplastic TPU, aminoresin crosslinked polyacrylate or polyester,
 polyisocyanate crosslinked polyester or polyacrylate, phenol/formaldehyde,
 urea/formaldehyde or melamine/formaldehyde resin, drying or non-drying alkyd resin, alkyd
 20 resin, polyester resin, acrylate resins cross-linked with melamine resin, urea resin,
 isocyanate, isocyanurate, carbamate, or epoxy resin, cross-linked epoxy resins derived
 from aliphatic, cycloaliphatic, heterocyclic or aromatic glycidyl compound, which are
 cross-linked with an anhydride or amine, polysiloxane, Michael addition polymer, amine,
 blocked amine with activated unsaturated or methylene compound, ketimine with activated
 25 unsaturated or methylene compound, polyketimine in combination with unsaturated acrylic
 polyacetoacetate resin, polyketimine in combination with unsaturated acrylic resin,
 radiation curable composition, epoxymelamine resin, organic dye, cosmetic product,
 cellulose-based paper formulation, photographic film paper, ink, and blends thereof.

Preferably, the light stabilized polymeric article is formed from a polyolefin
 30 homopolymer, copolymer, or terpolymer, and, more preferably, a homopolymer, copolymer,
 or terpolymer of polyethylene or polypropylene, where the polyethylene or polypropylene is
 a product of polymerization in the presence of at least one single site catalyst, at least one
 Ziegler-Natta catalyst, or both a Ziegler-Natta catalyst and at least one single site catalyst.

Other useful polymeric material that may be used to form the articles of the
 35 invention include, but are not limited to, polyamides, polyesters, polyacetals, and
 polyurethanes.

The present invention is also directed to a light stabilization additive composition, comprising at least one ortho hydroxy tris-aryl triazine light absorber and at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, as described above, and to a light stabilization additive concentrate, comprising from about 30 to about 98 percent, preferably from about 50 to about 95 percent, by weight of a polymeric resin, at least one ortho hydroxy tris-aryl triazine light absorber and at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, where the concentrate may be in the form of pellets, prills, or pastilles. The additive composition may be formed by spraying solutions of the light absorber and HALS, melt blending, extrusion, or by physical compaction.

The present invention is further directed to a method of forming a stabilized polymeric article. The method comprises blending a polymeric material with from about 50 to about 5,000 ppm of at least one ortho hydroxy tris-aryl triazine light absorber and from about 500 ppm to about 1.25 percent of at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, to form a stabilized polymeric composition, and forming an extruded or molded article or a biaxially oriented tape or film from the stabilized polymeric composition.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to compositions for stabilizing polymeric materials, such as molded or extruded articles, biaxially oriented tapes and films, and coatings, to prevent degradation from exposure to UV light, especially UV light having a wavelength of from about 290 to about 350 nm. It has been unexpectedly discovered that when from about 50 to about 5,000 ppm (parts per million) of an ortho hydroxy tris-aryl triazine and from about 500 ppm to about 1.25 percent of an oligomeric, polymeric, or high molecular weight HALS is blended with a polymeric material in a weight ratio of HALS to triazine of from about 3:1 to about 20:1, preferably from about 5:1 to about 10:1, and most preferably from about 6:1 to about 7.5:1, the polymeric material is protected from exposure to UV Light for a period of time substantially greater than afforded by any prior art light stabilizer composition containing a HALS, a UV light absorber, or a combination thereof.

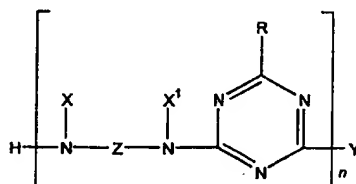
Preferably, the oligomeric, polymeric, or high molecular weight HALS has a molecular weight which is greater than about 500, and, preferably, greater than about

1,000. Suitable HALS are oligomers of the type disclosed in U.S. Patent No. 4,331,586, the contents of which are incorporated herein in their entirety.

HALS useful in the invention include, but are not limited to oligomers of formula (I)

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(I)

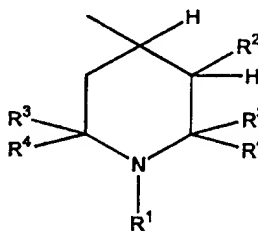


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wherein R is morpholino, C₁-C₈ alkylamine, di(C₁-C₈) alkylamine, pyrrolidyl, or cyclohexylamino, and is preferably morpholino or octylamine, X and X¹, which are the same or different, represent hydrogen, C₁-C₂₀ alkyl, or the radical (II)

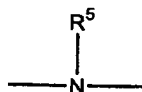
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20 (II)



25 where R¹ represents hydrogen, C₂-C₃ hydroxyalkyl, C₁-C₈ alkyl, hydroxyl, or oxyl; R² represents hydrogen, C₁-C₈ alkyl, or benzyl; R³ and R⁴, which may be the same or different, represent C₁-C₈ alkyl, benzyl, or phenethyl, or together with the carbon to which they are attached form a C₅-C₁₀ cycloalkyl; Z represents C₂-C₂₀ straight chained or branched alkylene, where the alkaline chain may be interrupted by oxy, thio, or

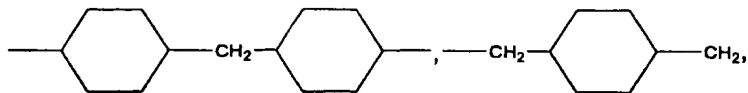
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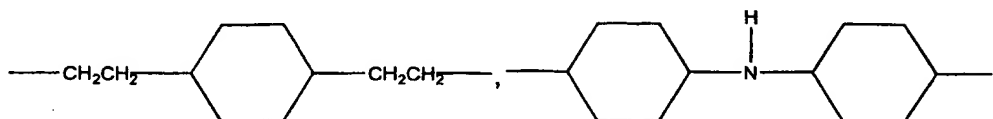
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radicals, wherein R⁵ represents hydrogen, C₁-C₂₀ alkyl, or the radical (II); C₅-C₁₀ cycloalkylene,

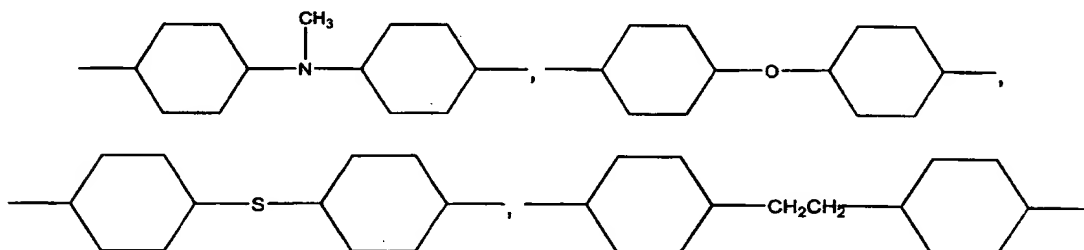
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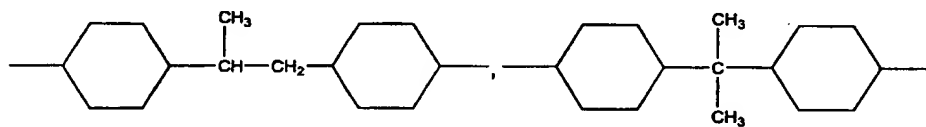
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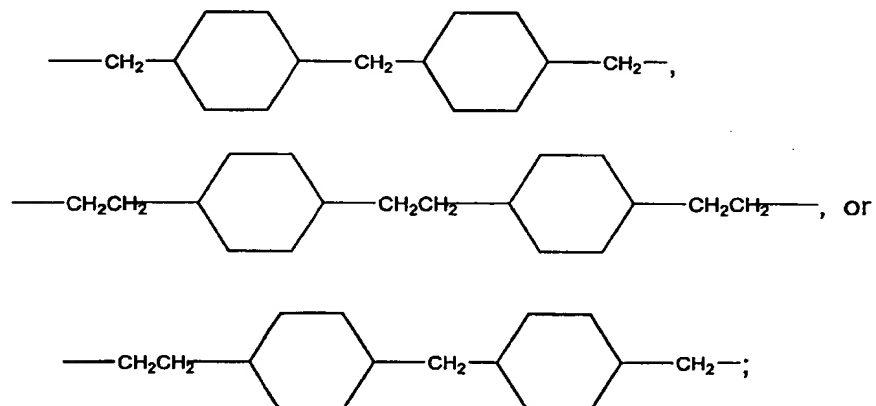
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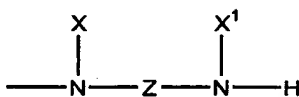


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C₈-C₁₂ arylene, or C₈-C₁₄ aralkylene; n is an integer greater than 1; and, Y represents a halogen atom, C₁-C₈ alkylamine, di(C₁-C₈) alkylamine, pyrrolidyl, morpholino, or

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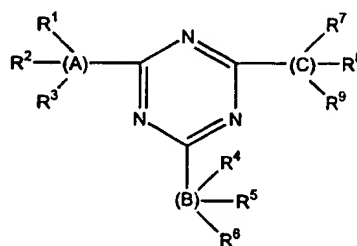
wherein X, X¹, and Z are as previously defined; with the proviso that at least one piperidinyl moiety of formula (II) is present in the repeating unit.

The preferred compositions of formula (I) are those wherein both X and X¹ are the moiety of formula (II). The especially preferred compositions of formula (I) are those wherein X and X¹ are 2,2,6,6-tetramethyl-4-piperidinyl, and Z is hexamethylene.

Ortho hydroxy tris-aryl triazines useful in the present invention as UV light absorbers are of the type disclosed in U.S. Patent No. 4,619,956, the contents of which are incorporated herein in their entirety. Generally, the triazine light absorber of the invention is of the formula (III)

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(III)



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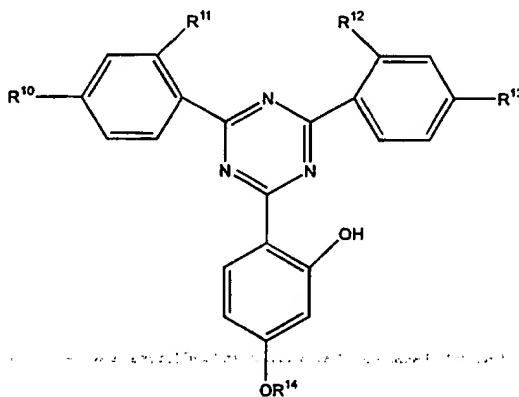
wherein A, B and C are each aromatic, at least one of A, B and C is substituted by a hydroxy group ortho of the point of attachment to the triazine ring, and each of R¹ through R⁹ is selected from the group consisting of hydrogen, hydroxy, alkyl, alkoxy, sulfonic, carboxy, halo, haloalkyl and acylamino.

20

Preferably, the triazine light absorber is of formula (IV)

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(IV)



30

where R¹⁰, R¹¹, R¹² and R¹³ are as described above for R¹ to R⁹, and are most preferably H or CH₃, and R¹⁴ is hydrogen or C₁ to C₁₈ alkyl with hydrogen, C₆ alkyl, and C₈ alkyl being most preferred.

Typically, a polymeric article, such as a molded or extruded article or a biaxially oriented tape or film, may be stabilized in the present invention by blending from about 50 to about 5,000 ppm of the triazine light absorber of the invention and about 500

ppm to about 1.25 percent of the HALS of the invention with a polymeric material used to form the article. The ratio of HALS to triazine light absorber is typically from about 20:1 to 3:1, preferably from about 10:1 to about 5:1, and most preferably from about 6:1 to about 7.5:1. Ideally, for polyolefins, the ratio is about 7:1, i.e., about 2,000 ppm HALS and about 300 ppm triazine, based on the weight of the polymeric material.

Although the HALS and triazine light absorber of the invention may be added to the polymeric material individually during processing of the polymeric material by any means known in the art, a mixture of the two components may be formed prior to processing. Typically, the additive composition of the invention is formed into pellets, prills, or pastilles comprising the HALS and UV light absorbers of the invention. This may be accomplished by melting the HALS and the triazine together, and extruding the mixture, spraying solutions of the two components together to form pellets or prills of the mixture upon the evaporation of the solvent, or by physical compaction.

The light stabilization additive composition of the invention may also be provided in the form of a concentrate containing from about 2 to about 70 percent, and preferably from about 5 to about 50 percent of the additive composition with the remainder comprising polymeric resin, and where the ratio of HALS to triazine light absorber is typically from about 20:1 to 3:1, preferably from about 10:1 to about 5:1.

The light stabilization additive composition of the invention may be used to stabilize thermoplastic substrates such as polyolefins, polyesters, polyethers, polyurethanes, polyamides, polystyrenes, high-impact polystyrenes, and the like, as molded articles, films, and the like. Preferably, the thermoplastic substrate is a polyolefin.

As used herein, the term Apolyolefin@ includes homopolymers of alpha olefins such as polyethylene, polypropylene, polybutadiene, polyisoprene, and the like; copolymers of alpha olefins, including ethylene-propylene copolymers, ethylene-butene, ethylene-hexene, and ethylene-octene copolymers, ethylene-vinyl acetate copolymers, styrene-butadiene copolymers, acrylonitrile-butadiene-styrene terpolyomers, and the like. Preferred polyolefins include polyethylene and polypropylene.

Other organic materials susceptible to degradation by the effects of light, the properties of which are improved by the incorporation therein of a compound of this invention, include polystyrene, natural and synthetic rubbers; the latter including, for example, homo-, co-, and terpolymers of acrylonitrile, butadiene and styrene, and blends thereof.

Optionally, the compositions may contain other additives, especially additives useful in polyolefins, such as antioxidants, supplemental light stabilizers,

plasticizers, flame retardants, antistatic and antislipping agents, fillers, dyes, pigments, and the like.

- Suitable antioxidants include those of the hindered phenol type, such as 2,6-di-t-butyl-p-cresol; 4,4'-bis(2,6-di-t-butylphenol);
- 5 tetrakis[methylene(3,5-ditert-butyl)-4-hydroxy-hydrocinnamate]]methane; 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione; 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-s-triazine-2,4,6-(1H,3H,5H)-trione; tris(2,4-ditert-butylphenyl)phosphite; bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite; 2[[2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[d,f][1,3,2]
- 10 dioxaphosphepin-6-yl]oxy]-N,N-bis[2[[2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-yl]oxy] ethanamine; oxidized bis(tallow alkyl) amines; 4,4'-bis(2,6-diisopropylphenol); 2,4,6-tri-t-butylphenol; 2,2'-thiobis(4-methyl-6-t-butyl phenol); octadecyl 2(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionate, etc; esters of thiodipropionic acid, such as
- 15 dilauryl thiodipropionate and distearyl thiodipropionate, etc; hydrocarbyl phosphites, such as triphenyl phosphite, trinonyl phosphite, diisodecyl pentaerythritol diphosphate, diphenyldecyl phosphite, etc; and combinations thereof.

- Suitable supplemental light stabilizers include those of the benzotriazole class, such as 2-(2'-hydroxy-5-t-octylphenyl)benzotriazole;
- 20 2(2'-hydroxy-3,5-di-t-butylphenyl)-5-chlorobenzotriazole; those of the hydroxybenzophenone type, such as 2-hydroxy-4-methoxybenzophenone; 2-hydroxy-4-octyloxybenzophenone; 2,2'-dihydroxy-4,4'-di-methoxybenzophenone; hindered phenol esters, such as n-hexadecyl 3,5-di-t-butyl-4-hydroxybenzoate, and -2,4'-di-t-butylphenyl 3,5-di-butyl-4-hydroxybenzoate; metal complexes of
- 25 2,2'-thiobis(4-t-octylphenol); nickel complexes of bis(4-t-octylphenyl)sulfone; nickel dibutyl dithiocarbamate; nickel salts of 4-hydroxy-3-di-t-butylbenzyl phosphoric acid monoalkyl esters where alkyl is methyl, ethyl, propyl, butyl, etc; nickel complex of 2-hydroxy-4-methylphenyl undecyl ketone oxime, etc.

- Polymeric articles that may be protected from UV light with the present
- 30 invention include, but are not limited to molded or extruded articles; coatings; tapes; and films. The articles may be formed by extrusion, sheet extrusion, injection molding, blow molding, injection blow molding, rotational or roto-molding, calendering, thermoforming, compression molding, vacuum molding, pressure molding, reaction injection molding, and other similar techniques known in the art. In addition, coatings may be applied by powder
- 35 coating, extrusion coating, electrocoating, spraying, dipping, and other similar techniques known in the art.

EXAMPLES

The following non-limiting examples are merely illustrative of the preferred embodiments of the present invention, and are not to be construed as limiting the invention, the scope of which is defined by the appended claims.

Example 1.

Test samples were prepared as follows: Irganox 1010 (0.5 g), an antioxidant, Irgafos 168 (1.0 g), a phosphite as a processing stabilizer, and zinc stearate (0.25 g) were dry blended with LLDPE (low density polyethylene) and the UV stabilizers listed in TABLE 1. The resulting formulations were compounded at 175EC on a one and one quarter inch single screw extruder, and converted to tensile bars by injection molding at 200EC with a mold temperature of 60EC. The tensile bars were exposed in an Atlas Ci65 WOM with water spray, and elongation at break was measured as a function of time. The results, which are provided as the percent elongation at break, are provided in TABLE 1, where an elongation of less than 50 percent is considered failure.

TABLE 1

Formulation	0 hrs.	4,000 hrs.	6,000 hrs.	8,000 hrs.	10,000 hrs.	12,00 0 hrs.	14,00 0 hrs.	16,000 hrs.
Chimassorb 944 (0.3%) ¹	514	551	486	361	218	118	67	46
Tinuvin 622 (0.3%) ²	509	226	152	61	43			
Cyasorb7 UV 3346 light stabilizer (0.3%) ³	501	548	479	410	301	90	85	45

Cyasorb7 UV 3346 light stabilizer (0.2%) Cyasorb7 UV 1164 (0.03%) ⁴	502	570	483	440	411	442	527	402
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1. N,N-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexane diamine, polymer with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentamine
2. Dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol
- 5 3. Poly[(6-morpholino-s-triazine-2,4-diyl)]
[2,2,6,6,-tetramethyl-4-piperidyl]imino]-hexamethylene
[(2,2,6,6,-tetramethyl)-4-piperidyl]imino]
4. A compound of formula (IV), where R¹⁰, R¹¹, R¹² and R¹³ are all methyl, and R¹⁴ is C₈H₁₇.

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As can be clearly seen from the data, the composition light stabilized by the invention is far superior to the prior art compositions, providing protection from UV light for as long as 16,000 hours, at which point the composition still maintains 80 percent of its initial elongation. In contrast, the elongation at break for the compositions light stabilized by the prior art compositions begins to dramatically decrease after exposures to UV light of only 4,000 to 10,000 hours, with failure, i.e., less than 50 percent elongation at break, occurring at 10,000 to 16,000 hours.

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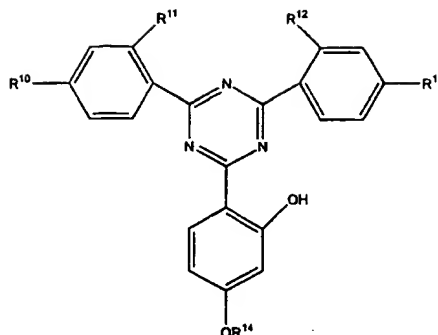
Example 2.

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The ability of the light stabilizing compositions disclosed in U.S. patent No. 4,619,956 to Susi ("the '956 patent") to protect polymeric materials from degradation on exposure to UV light was compared to that of the compositions of the present invention.

The '956 patent exemplifies the effect of prolonged exposure of polymeric materials to UV light, where each sample of polymeric material contains equal amounts of a light stabilizing compositions comprising a triazine light absorber of formula

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where R^{10} , R^{11} , R^{12} and R^{13} are CH_3 , and R^{14} is C_8 alkyl, and a commercially available
 10 HALS, i.e., Tinuvin7 765, Tinuvin7 440, Tinuvin7 900, and Sanduvor7 3050. Upon
 exposure to alternate cycles of 8 hours of exposure to UV light followed by no UV for 4
 hours, the sample of polymeric material show a pronounced decrease in gloss and an
 increase in yellowness after periods of from 1,200 to 2,400 hours. In contrast, polymeric
 material comprising the compositions of the invention retain useful properties for at least
 15 16,000 hours, clearly demonstrating the superiority of the compositions of the invention
 when compared to compositions containing equal amounts of HALS and triazine.

Example 3.

A polyamide light stabilized by blending the polyamide with from about 50 to
 20 about 5,000 ppm of an ortho-hydroxy tris-aryl triazine light absorber and from about 500
 ppm to about 1.25 percent of an oligomeric, polymeric, or high molecular weight HALS
 having a molecular weight of at least 500, where the weight ratio of HALS to triazine light
 absorber is from about 3:1 to about 20:1, maintains useful physical properties when
 exposed to UV light for a significantly longer period of time than polyamide blended with
 25 prior art light stabilizer compositions. Good results are obtained when the weight ratio of
 HALS to triazine light absorber is from about 5:1 to about 10:1.

Example 4.

A polyester light stabilized by blending the polyester with from about 50 to
 30 about 5,000 ppm of an ortho-hydroxy tris-aryl triazine light absorber and from about 500
 ppm to about 1.25 percent of an oligomeric, polymeric, or high molecular weight HALS
 having a molecular weight of at least 500, where the weight ratio of HALS to triazine light
 absorber is from about 3:1 to about 20:1, maintains useful physical properties when
 exposed to UV light for a significantly longer period of time than polyester blended with
 35 prior art light stabilizer compositions. Good results are obtained when the weight ratio of
 HALS to triazine light absorber is from about 5:1 to about 10:1.

Example 5.

A polyacetal light stabilized by blending the polyacetal with from about 50 to about 5,000 ppm of an ortho-hydroxy tris-aryl triazine light absorber and from about 500 ppm to about 1.25 percent of an oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least 500, where the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, maintains useful physical properties when exposed to UV light for a significantly longer period of time than polyacetal blended with prior art light stabilizer compositions. The best results are obtained when the weight ratio of HALS to triazine light absorber is from about 5:1 to about 10:1..

Example 6.

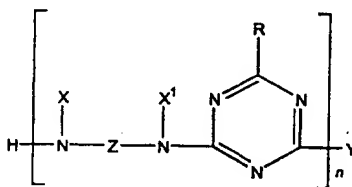
A polyurethane light stabilized by blending the polyurethane with from about 50 to about 5,000 ppm of an ortho-hydroxy tris-aryl triazine light absorber and from about 500 ppm to about 1.25 percent of an oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least 500, where the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, maintains useful physical properties when exposed to UV light for a significantly longer period of time than polyurethane blended with prior art light stabilizer compositions. Good results are obtained when the weight ratio of HALS to triazine light absorber is from about 5:1 to about 10:1.

While it is apparent that the invention disclosed herein is well calculated to fulfill the objects stated above, it will be appreciated that numerous modifications and embodiments may be devised by those skilled in the art. Therefore, it is intended that the appended claims cover all such modifications and embodiments that fall within the true spirit and scope of the present invention.

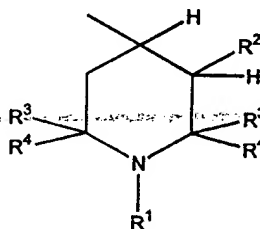
THE CLAIMS

What is claimed is:

1. A polymeric article, comprising a polymeric material, from about 50 to about 5,000 ppm of at least one ortho-hydroxy tris-aryl triazine light absorber, and from about 500 ppm to about 1.25 percent of at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least 500, wherein the weight ratio of HALS to triazine is from about 3:1 to about 20:1, and wherein the polymeric article is a molded article, an extruded article, or a biaxially oriented tape or film.
2. The polymeric article of claim 1, wherein the ratio of HALS to triazine light absorber is from about 5:1 to about 10:1.
3. The polymeric article of claim 1, wherein the ratio of HALS to triazine light absorber is in the range of from about 6:1 to about 7.5:1.
4. The polymeric article of claim 1, wherein the HALS is an oligomer of formula (I)



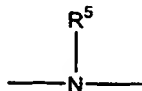
- wherein R is morpholino, C₁-C₈ alkylamine, di(C₁-C₈) alkylamine, pyrrolidyl, or cyclohexylamine, X and X¹, which are the same or different, and are hydrogen, C₁-C₂₀ alkyl, or a radical of formula (II)



- wherein R₁ represents hydrogen, C₂-C₃ hydroxyalkyl, C₁-C₈ alkyl, hydroxyl, or oxyl; R² represents hydrogen, C₁-C₈ alkyl, or benzyl; R³ and R⁴, are the same or different, and are C₁-C₈ alkyl, benzyl, or phenethyl, or form a C₅-C₁₀ cycloalkyl; Z is a straight chained or

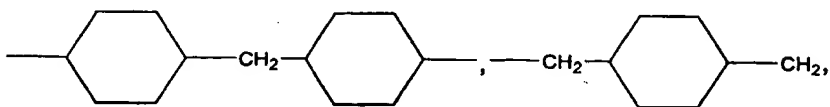
branched C₂-C₂₀ alkylene or a straight chained or branched C₂-C₂₀ alkylene chain interrupted by at least oxy, thio, or

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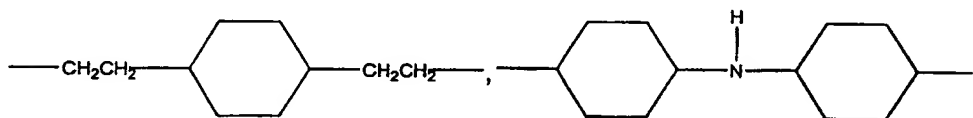


radical, wherein R⁵ is hydrogen, C₁-C₂₀ alkyl, or the radical of formula (II); C₅-C₁₀ cycloalkylene,

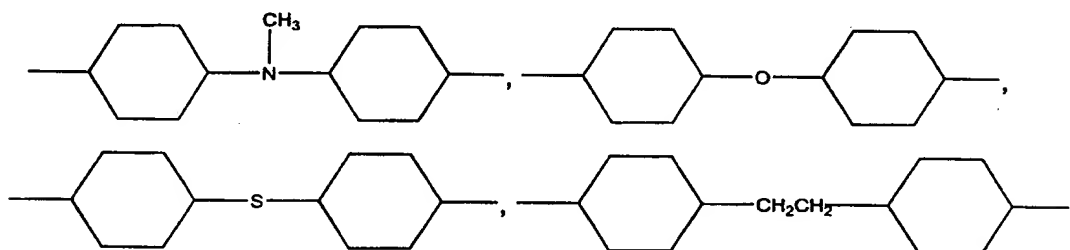
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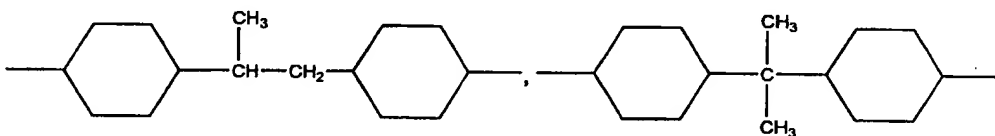
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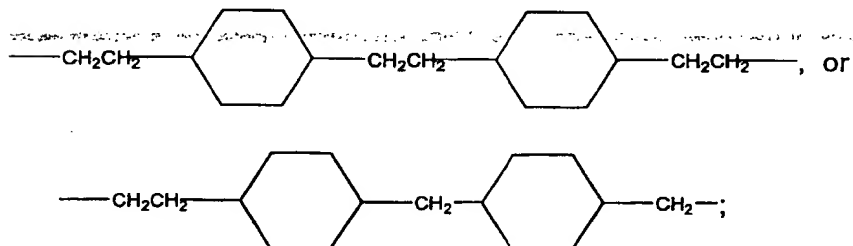
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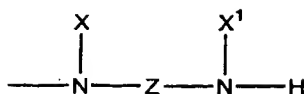


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C₆-C₁₂ arylene, or C₈-C₁₄ aralkylene; n is an integer greater than 1; and Y is a halogen atom, C₁-C₈ alkylamine, di(C₁-C₈) alkylamine, pyrrolidyl, morpholino, cyclohexylamine, or

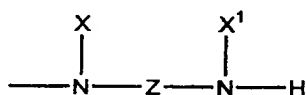
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wherein X, X¹, and Z are as previously defined; with the proviso that at least one of X and X¹ is of formula (II).

10. 5. The polymeric article of claim 4, wherein X and X¹ are the same or different, and are of formula (II), wherein R is morpholino or octylamine, R¹ is H or CH₃, R² is H, R³ and R⁴ are CH₃, Z is C₆H₁₂, and Y is morpholino, octylamine, or

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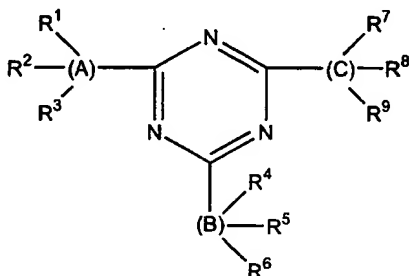


wherein X, X¹, and Z are as previously defined.

- 20 6. The polymeric article of claim 1, wherein the HALS is selected from the group consisting of Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperdiny)sebacate, dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol, a blend of dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol and
- 25 N,N-bis(2,2,6,6-tetramethyl-4-piperidiny)-1,6-hexane diamine, polymer with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentamine, 1,3,5-triazine-2,4,6-triamine, N,N==[1,2-ethanediylbis
- 30 [[[(4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazine-2-yl]imino]-3,1propanediyl]]-bis[N=N==dibutyl-N=N==bis(1,2,2,6,6-pentamethyl-4-piperidiny), 1,3,5-triazine-2,4,6-triamine, N,N==[1,2-ethanediylbis
- [[[(4,6-bis[butyl(1-cyclohexyloxy-2,2,6,6-tetraamethyl-4-piperidiny)amino]-1,3,5-triazine-2-yl]imino]-3,1-propanediyl]]-bis[N=N==dibutyl-N=N==bis(1,2,2,6,6-pentamethyl-4-piperidiny), 1,3,5-triazine-2,4,6-triamine, N,N==[1,2-ethanediylbis
- 35 [[[(4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-2-yl]imino]-3,1propanediyl]]-bis[N=N==dibutyl-N=N==bis(1,2,2,6,6-pentamethyl-4-piperidiny), N,N-bis(2,2,6,6-tetramethyl-4-piperidiny)-1,6-hexane diamine polymer with

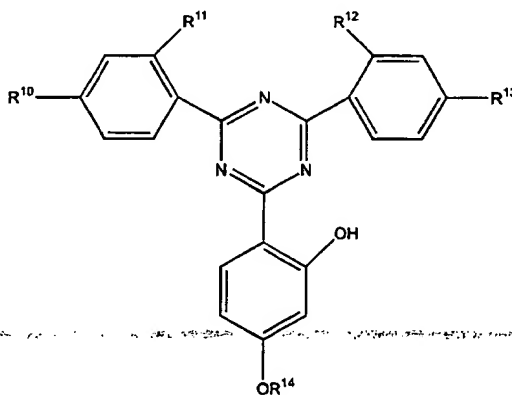
- 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentamin ,
 poly-methylpropyl-3-oxy-(4(2.2.6.6-tetramethyl)piperidinyl) siloxane,
 poly-methylpropyl-3-oxy-(4(1,2.2.6.6-pentamethyl)piperidinyl)siloxane,
 polyalkyl-1-oxa-diazaspirodecane products of a reaction of
 5 tetramethyl-7-oxa-3,20-diaza-21-oxo-dispiro (5.1.11.12)heneicosane with epichlorohydrin,
 1,3-propanediamine,N,N--1,2-ethanediylbis-,polymer with 2,4,6-trichloro-1.3.5-triazine,
 reaction products with N-butyl-2,2,6,6-tetramethyl-4-piperidinamine.

7. The polymeric article of claim 1, wherein the triazine light absorber is
 10 of formula (III)



- 15 wherein A, B and C are each aromatic, at least one of A, B and C is substituted by a
 hydroxy group ortho of the point of attachment to the triazine ring, and each of R¹ through
 R⁹ is selected from the group consisting of hydrogen, hydroxy, alkyl, alkoxy, sulfonic,
 20 carboxy, halo, haloalkyl and acylamino.

8. The polymeric article of claim 7, wherein the triazine light absorber is
 of formula (IV)



- 25 where R¹⁰, R¹¹, R¹² and R¹³ are the same or different, and are individually selected from
 the group consisting of hydrogen, hydroxy, alkyl, alkoxy, sulfonic, carboxy, halo, haloalkyl
 and acylamino, and R¹⁴ is hydrogen or C₁ to C₁₈ alkyl.
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9. The polymeric article of claim 8, wherein R^{10} , R^{11} , R^{12} and R^{13} H or CH_3 , and R^{14} is hydrogen, C_6H_{13} , or C_8H_{17} .

10. The polymeric article of claim 7, wherein the triazine light absorber is
5 selected from the group consisting of
2-(4,6-Diphenyl-1,3,5-triazine-2-yl)-5-(hexyl)oxy-phenol,
2-(4-((2-hydroxy-3-dodecyloxypropyl)-oxyl-2-hydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,
3,5-triazine, 2-(4-((2-hydroxy-3-tridecyloxypropyl)-oxyl-2-hydroxyphenyl)-
4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, and
10 2-(4-((2-hydroxy-3-isooctyloxypropyl)-oxyl-2-hydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,
3,5-triazine.

11. The polymeric article of claim 1, wherein the polymeric article is a
molded or extruded article having a thickness of no less than about 1 mm.

12. The polymeric article of claim 1, wherein the polymeric material is
selected from the group consisting of polyolefins, polyesters, polyethers, polyketones,
polyamides, natural and synthetic rubbers, polyurethanes, polystyrenes, high-impact
polystyrenes, polyacrylates, polymethacrylates, polyacetals, polyacrylonitriles,
20 polybutadienes, polystyrenes, ABS, SAN (styrene acrylonitrile), ASA (acrylate styrene
acrylonitrile), cellulosic acetate butyrate, cellulosic polymers, polyimides, polyamideimides,
polyetherimides, polyphenylsulfide, PPO, polysulfones, polyethersulfones,
polyvinylchlorides, polycarbonates, polyketones, aliphatic polyketones, thermoplastic
TPU's, aminoresin crosslinked polyacrylates and polyesters, polyisocyanate crosslinked
25 polyesters and polyacrylates, phenol/formaldehyde, urea/formaldehyde and
melamine/formaldehyde resins, drying and non-drying alkyd resins, alkyd resins, polyester
resins, acrylate resins cross-linked with melamine resins, urea resins, isocyanates,
isocyanurates, carbamates, and epoxy resins, cross-linked epoxy resins derived from
aliphatic, cycloaliphatic, heterocyclic and aromatic glycidyl compounds, which are
30 cross-linked with anhydrides or amines, polysiloxanes, Michael addition polymers, amines,
blocked amines with activated unsaturated and methylene compounds, ketimines with
activated unsaturated and methylene compounds, polyketimines in combination with
unsaturated acrylic polyacetoacetate resins, polyketimines in combination with unsaturated
acrylic resins, radiation curable compositions, epoxymelamine resins, organic dyes,
35 cosmetic products, cellulose-based paper formulations, photographic film paper, ink, and
blends thereof.

13. The polymeric article of claim 1, wherein the polymeric material is a polyolefin homopolymer, copolymer, or terpolymer.

5 14. The polymeric article of claim 13, wherein the polymeric material is a homopolymer, copolymer, or terpolymer of polyethylene or polypropylene.

15 15. The polymeric article of claim 14, wherein the polyethylene or polypropylene is a product of polymerization in the presence of at least one Ziegler-Natta catalyst.

16 16. The polymeric article of claim 14, wherein the polyethylene or polypropylene is a product of polymerization in the presence of at least one single site catalyst.

17 17. The polymeric article of claim 14, wherein the polyethylene or polypropylene is a product of polymerization in the presence of both a Ziegler-Natta catalyst and at least one single site catalyst.

20 18. The polymeric article of claim 1, wherein the polymeric material is selected from the group consisting of polyamides, polyesters, polyacetals, and polyurethanes.

25 19. The polymeric article of claim 18, wherein the weight ratio of HALS to triazine light absorber is from about 5:1 to about 10:1.

20. The polymeric article of claim 18, wherein the weight ratio of HALS to triazine light absorber is from about 6:1 to about 7.5:1.

30 21. A light stabilization additive composition, comprising at least one ortho hydroxy tris-aryl triazine light absorber and at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1.

35 22. A light stabilization additive concentrate, comprising from about 30 to about 98 percent by weight of a polymeric resin, at least one ortho hydroxy tris-aryl

triazine light absorber and at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1.

5 23. The light stabilization additive concentrate of claim 22, wherein the additive concentrate is in the form of pellets, prills, or pastilles.

 24. The light stabilization additive concentrate of claim 22, wherein the resin is present in an amount from about 50 to about 95 percent by weight.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/06862

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K5/00 //(C08K5/00, 5:3492, 5:3435)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	EP 0 889 085 A (CIBA) 7 January 1999 (1999-01-07) examples 22, 30	1, 7, 8, 11-14
A	----- CHEMICAL ABSTRACTS, vol. 130, no. 14, 5 April 1999 (1999-04-05) Columbus, Ohio, US; abstract no. 183208, PATERNA ET AL.: "BALANCING THE COLOR AND PHYSICAL PROPERTY RETENTION OF POLYOLEFINS THROUGH THE USE OF HIGH PERFORMANCE STABILIZER SYSTEMS" XP002108670 abstract & "INT. CONF. ADDIT. POLYOLEFINS" 1998, SOCIETY OF PLASTICS ENGINEERS, BROOKFIELD, CONN. page 231 - page 243 ----- -/-	1, 13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

15 July 1999

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/06862

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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